

The Absorption Spectra of Lithium and Cæsium.

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(Communicated by Sir J. J. Thomson, F.R.S. Received January 20,—

Read March 9, 1911.)

In a paper* communicated to the Royal Society in February, 1910, I gave the results of measurements of absorption lines for the three alkali metals, potassium, rubidium, and cæsium. Up to that time I had not been able to obtain the corresponding spectrum for lithium vapour. This was owing to the fact that lithium vaporises at a considerably higher temperature than the other alkali metals, and at the high temperatures required for a sufficient density of vapour the lithium attacks the material of all tubes which I was able to use. Steel, brass, platinum, glass, silica, carbon are all attacked, and no satisfactory photographs could be obtained. Recently, however, by using a relatively large quantity of lithium in a steel tube sufficient vapour was obtained to give an absorption spectrum showing 27 lines of the principal series. The method was the same as that described in the paper referred to, with the exception that a second steel tube was placed in the outer steel absorption tube. This was simply for the protection of the outer tube, which would probably collapse after being acted on by lithium vapour at the bright red heat to which it was raised. The source of light used was the cadmium spark, as the limit of the series is so much further in the ultra-violet than in the case of the other alkali metals.

The following table gives the wave-lengths and oscillation frequencies for the complete series of lithium lines. (See Table I opposite.)

The lines 1 to 9 are given by Kayser, 10 to 27 are new.

In addition to the absorption spectrum consisting of these lines of the principal series, there is a fluted region corresponding to the similar region in the cases of sodium and potassium vapours. This extends over the wave-lengths between about 4500 and 5500, and corresponds fairly closely in position with the sodium fluted region. The fluted region is, in appearance, like those in the cases of sodium and potassium, and appears under similar circumstances—when the vapour is fairly dense, giving a broadened line for the first member of the principal series. It consists of a large number of fine lines, grouped so as to show under small dispersion bands with fairly definite edges in the central position of the spectrum—at the two ends the appearance of sharp edges is lost.

* 'Roy. Soc. Proc.,' A, vol. 83, p. 421.

Table I.

	λ .	Possible errors.	$10^8 \lambda^{-1}$ in <i>vacuo</i> .	O—C.
1	6708.2		14902.7	
2	3232.77		30923.7	
3	2741.39		36466.4	
4	2562.60		39010.6	
5	2475.13		40389.2	
6	2425.55		41214.7	
7	2394.54		41748.5	
8	2373.9	0.2	42111.4	+0.1
9	2359.4	0.2	42370.2	+0.2
10	2348.5	0.2	42568	0
11	2340.5	0.2	42713	+0.1
12	2334.3	0.2	42827	+0.1
13	2329.0	0.3	42924	—0.3
14	2325.2	0.2	42994	—0.1
15	2321.9	0.3	43055	—0.2
16	2319.3	0.3	43103	—0.2
17	2317.1	0.2	43144	—0.1
18	2315.2	0.2	43180	—0.2
19	2313.6	0.4	43210	—0.2
20	2312.2	0.4	43236	—0.3
21	2311.1	0.2	43256	—0.1
22	2310.0	0.2	43277	—0.2
23	2309.0	0.2	43296	—0.2
24	2308.3	0.2	43309	—0.2
25	2307.5	0.2	43324	—0.2
26	2307.0	0.3	43333	—0.1
27	2306.5	0.3	43343	0

The table contains in the second column the estimated possible errors in the determinations of the wave-lengths. Hicks* has emphasised the importance of recording the possible errors in wave-length determinations, and, although these determinations do not make any pretence at great accuracy, the possible errors for each wave-length have been estimated. They vary through the series owing to the differences in the situation of lines; for example, the two lines 19 and 20 of the series have possible errors of 0.4 given to them owing to the fact that they occur close to the cadmium line of wave-length 2313, and where we have absorption lines close to an emission line of the source of light—in this case the cadmium spark—the exact position of the centre of the line is difficult to determine. An attempt was made to obtain the absorption spectrum with another source than the cadmium spark, but without success—the cadmium spark seems to give the best intensity of light so far in the ultra-violet as the lines under discussion. The lines 8 and 9 were measured again. The values given by Kayser are due to Liveing and Dewar, and no estimate of error is given. The values obtained by me are the same as those of Liveing and Dewar.

* 'Phil. Trans.,' vol. 210, p. 58.

Various formulæ have been suggested for series lines. Those of Rydberg and Kayser and Runge have been shown to be not sufficiently accurate for representing observed values, and several modifications of these have been brought forward. The most promising of these is perhaps that of Hicks,* which is a modified Rydberg formula. This formula gives n , the oscillation frequency, *i.e.* the number of waves per centimetre, in the following form—

$$n = A - N / \left(m + \mu + \frac{\alpha}{m} \right)^2,$$

where N is the universal Rydberg constant, 109675, and m takes the values 1, 2, 3, etc., for the different lines of the series, the other quantities being constants for the particular substance. With the values of these constants found by Hicks for lithium, we find very good agreement for the calculated and observed values of the wave-lengths; in the last column of Table I there are given the differences between the observed and calculated wave-lengths under the heading O—C. The agreement is seen to be within the estimate of the possible error, but there is an indication that the observed values are all smaller than the calculated values. This would be accounted for by a value of the constant A , which is too small. The possible error in this constant, 43482.20, is 11.18 according to Hicks. The maximum amount allowable would make in the wave-lengths a difference of 0.06 or 0.1 to the nearest tenth of an Ångström unit. This would still leave over a small negative error in the values O—C, which may fairly be accounted for by the nature of the lines measured; they are faint absorption lines, and so not so sharp as good emission lines.

This series for lithium is interesting, as on the lines of work of Hicks, already referred to, the series is of a different type from the principal series of the other alkali metals. This difference is discussed by Hicks in the paper already cited. From the physical point of view, however, the series seems to behave just like the series in the cases of the other alkali metals. The set of lines appears under very similar conditions as absorption lines, taking account of the higher temperature required for volatilisation of the lithium, and the series is accompanied by the channelled space spectrum as is the case with sodium and potassium. The earlier members of the series are easily reversed in the arc, and anomalous dispersion effects appear in transmitted light for wave-lengths in the neighbourhood of the series lines. In these respects the physical characteristics of these lines are exactly like those exhibited by the corresponding lines in the cases of the other metals.

* *Loc. cit.*

It is difficult then to see what the meaning of the difference in type as discovered by Hicks can be.

It may be remarked in this connection that the values for the constants A of the Hicks formula, that is the wave numbers of the heads of the series, viz., Li 43482, Na 41446, K 35006, Rb 33687, Cs 31400, continually decrease as the atomic weights increase, so that we cannot attach too much importance to the fact that the first members of these series do not fall into such regular order, the number for lithium being apparently out of place. It may also be mentioned that the order into which the wave numbers of the first members of the series fall for the elements other than lithium does not show any close relation to the atomic weights.

In a note from Prof. Hicks he has pointed out that in the wave-lengths for the cæsium principal series lines published in a paper I communicated to the Royal Society in January, 1910, there are probably some errors in the determinations, as some of the later lines of the series show departures from the values which seem probable as calculated from his formula. I have made a re-determination of these lines from photographs of the absorption spectra for cæsium vapour set free by the action of sodium and potassium on the chloride of cæsium. I have not been able to obtain metallic cæsium, and the presence of the vapour of the other metals rather obscures the absorption lines due to the metal. With some better photographs a few more lines have been measured, extending the list to 24 for the principal series. With the vapour of cæsium itself there is not much doubt that a considerably larger number of the lines could be observed.

The following table gives the re-determinations of wave-lengths for the lines from No. 8 of the series; 22, 23, and 24 are new lines. With regard to the accuracy of determination of those measurements, it is not so good as for the lithium lines, as there is considerably more dispersion in the region occupied by these latter, so that we can estimate the possible error as 0.5 of an Ångström unit. In the third column is given the difference between the observed and calculated values of the wave-length, the calculated value being obtained from the Hicks formula,

$$n = 31400.16 - N / \left(m + 1.450967 - \frac{0.090077}{m} \right)^2.$$

The comparison spectrum for this purpose was that of the iron arc.

It will be noticed that all the differences in the third column are of the same sign; a change in the constant A of the Hicks formula, sufficient to make a change of 0.5 in the limiting wave-length, would bring all these observed wave-lengths into agreement with the formula. The possible error, however,

Table II.

<i>m.</i>	λ .	O—C.
8	3313·5	—0·3
9	3288·9	—0·3
10	3270·4	—0·7
11	3256·6	—0·7
12	3245·9	—0·6
13	3237·8	—0·2
14	3230·6	—0·6
15	3224·6	—0·9
16	3220·3	—0·5
17	3216·4	—0·5
18	3212·9	—0·6
19	3210·1	—0·5
20	3207·7	—0·1
21	3205·6	—0·4
22	3204·0	—0·2
23	3202·4	—0·1
24	3200·7	—0·4

in A of the formula cannot be determined, for the observations used in its calculation have not their possible errors ascribed to them.

Dispersion in Vapours of the Alkali Metals.

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[PLATES 6 AND 7.]

In the 'Proceedings' of the Royal Society, A, vol. 84, p. 209, I gave an account of experiments with Potassium vapour, which had for their object the determination of the dispersion curve for the vapour. The effect of the first three pairs of lines of the principal series was quantitatively estimated, and it appeared that certain conclusions could be drawn as to the numbers of systems taking part in the absorption of light. The present communication deals with further experiments of the same kind with vapours of Sodium and Rubidium, and again with the vapour of potassium, as far as regards a temperature effect, which will be discussed later. The experiments were made possible by a grant from the Royal Society, which enabled me to obtain metallic rubidium, and I am glad to take this opportunity of thanking the Government Grant Committee.